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Complementary ligands direct the formation of a calix[8]arene-supported ferromagnetic Mn^{IV}Mn^{III} dimer†**

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Abstract

A combination of complementary ligands, *p-tert*-butylcalix[8]arene (TBC[8]) and phenyl salicylaldoxime (Ph-saoH₂) have been utilised in the facile synthesis of a Mn^{III}Mn^{IV} dimer. Magnetic measurements reveal ferromagnetic exchange between the two metal ions.

Introduction

The synthesis of paramagnetic metal clusters that display interesting magnetic properties is now an intensely active area of research. Of particular importance is the sub-field of single molecule magnetism.^{1a} Generally SMMs are composed of a polymetallic cluster stabilised by polytopic organic ligands. The preparation of such species often relies on the serendipitous assembly of the appropriate components, and consequently controlled formation of SMMs remains somewhat elusive.^{1b} As chemists we are most interested in the various synthetic factors that govern the nuclearity of cluster formation, the resultant topology and the related mechanisms by which the magnetic cluster properties can be optimised. A degree of control can be gained by examination of the myriad of literature compounds and exploitation of the known coordination modes of the component ligand moieties. The choice of ligand is therefore of crucial importance in cluster formation.

A class of ligand that has recently been exploited in our laboratories, and in others,² in the synthesis of magnetically interesting compounds, are the *p-tert*-butylcalix[*n*]arenes (TBC[*n*]) or the related calix[*n*]arenes (C[*n*]) (Fig. 1A). C[*n*]s are cyclic polyphenolic macrocycles that adopt well defined conformations as a consequence of hydrogen bonding interactions between phenolic hydroxyl groups.³ The cone conformer of TBC[4] was identified as an attractive molecule for binding a transition metal or lanthanide ion, and it was proved thus with the isolation of a series of [Mn^{III}₂Mn^{II}₂(TBC[4])₂] SMMs (Fig. 1B).^{2b,c} Further investigations yielded [Mn^{III}₄Ln^{III}₄(C[4])₄] cages that are magnetic refrigerants or SMMs depending on the lanthanide employed;^{2d,e} other important examples being the mixed metal [Fe^{III}₂Ln^{III}₂(TBC[4])₂]^{2f} and the octahedral [Ln^{III}₆(TBC[4])₂] complexes.^{2g} Recently a ferromagnetic [Mn₅] cluster, [Mn^{III}₃Mn^{II}₂(TBC[4])₂(hmp)₂] (Hhmp = 2-(hydroxymethyl)pyridine),^{2h} has been synthesised using complementary ligands that each display well-defined coordination motifs.

In contrast to the (now) many examples of metal clusters supported by TBC[4], the corresponding chemistry of magnetically interesting metal clusters supported by its larger octameric analogue is less developed,⁴ despite TBC[8] (Fig. 1A, *n* = 8) also being a readily accessible synthetic target. A survey of the Cambridge Structural Database (CSD) for TBC[*n*] and at least one transition metal found ~450 hits for TBC[4], but only ~20 hits for TBC[8]. This may in part be due to the additional

conformational flexibility of the larger calixarene, meaning that controlling these systems is inherently more difficult.

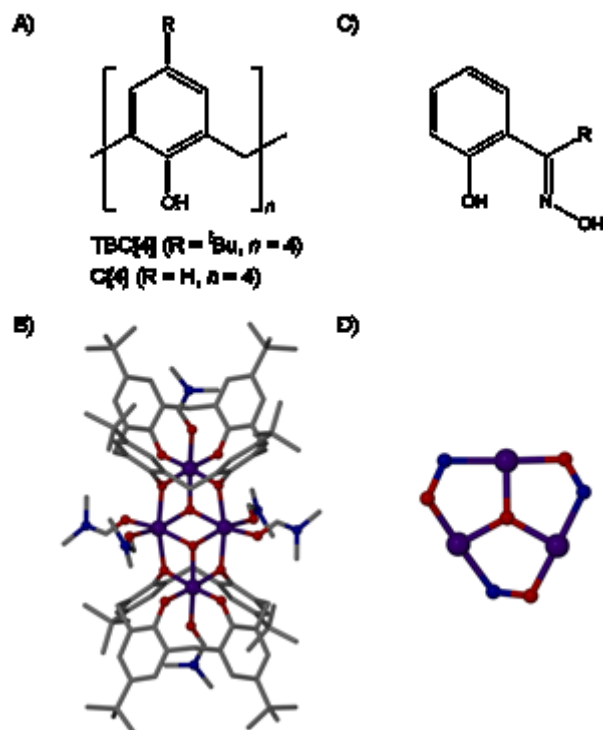


Figure 1. A) Generic C[n] structure. B) Structure of a [Mn^{III}₂Mn^{II}₂(TBC[4])₂] SMM. C) Structure of R-saoH₂ and the triangular [Mn^{III}₃O(N-O)₃]⁺ fragment it normally stabilises (D). Colour code: C grey; O red; N blue; Mn purple.

A second class of ligand extensively employed in the synthesis of paramagnetic metal clusters are the derivatised salicylaldoximes (R-saoH₂, Fig. 1C),⁵ which tend to assemble M(III) ions into structures based upon the triangular [M^{III}₃O(R-sao)₃]⁺ motif (Fig. 1D). A salient feature of the Mn(III) chemistry is that the pairwise magnetic exchange is dependent upon the relative twisting of the Mn-N-O-Mn moiety, and this is controlled by the nature of the R-substituent on the oximic carbon atom.⁶ Disruption of the formation of [Mn^{III}₃O(R-sao)₃]⁺ building blocks by addition of complementary/competing co-ligands should therefore lead to a diverse range of molecules with fascinating structural and magnetic properties.^{2h} Indeed, herein we report a rare example of an oxime-bridged manganese dimer housed inside a TBC[8] scaffold, assembled from the complementary ligands Ph-saoH₂ and TBC[8].

Reaction of Mn(NO₃)₂·4H₂O, TBC[8] and Ph-saoH₂ in a basic solution of DMF/MeOH produces

black crystals of $[\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}(\text{TBC}[8]\text{-4H})(\text{Ph-sao})(\mu\text{-OMe})(\text{dmf})_2]\cdot 5\text{dmf}$, (**1**·5dmf; Figure 2), upon standing over several days.† The crystals were found to be in a triclinic cell and structure solution was performed in the space group *P*-1.

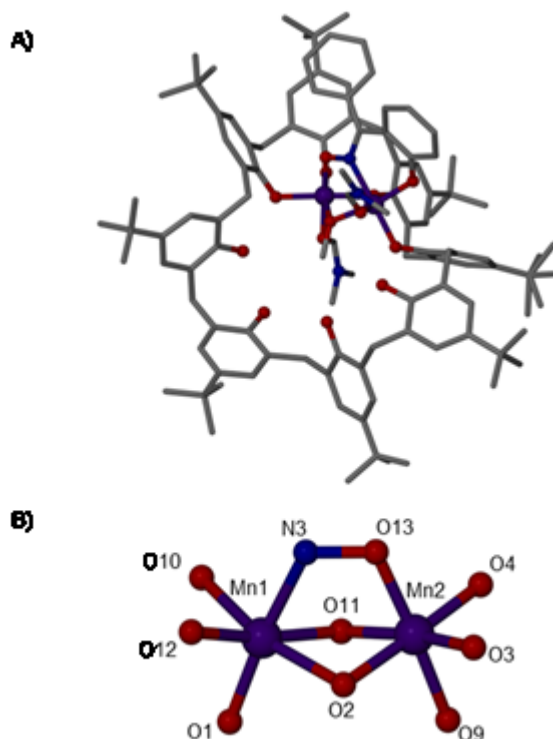


Figure 2. A) Single crystal X-ray structure of **1**. B) Magnetic core and coordination spheres of Mn atoms in **1**. Non-coordinating solvents and hydrogen atoms are omitted for clarity. Colour code: C grey; O red; N blue; Mn purple.

The metal core of **1** is composed of one Mn^{3+} (Mn1) ion and one Mn^{4+} (Mn2) ion. Mn1 exists in a distorted octahedral geometry with the equatorial sites occupied by a TBC[8] oxygen atom (O1), the Ph-sao^{2-} phenolic oxygen and oximic nitrogen atoms (O12 and N3) and a μ -bridging methoxide oxygen (O11, $\text{Mn1-O11-Mn2} = 99.8^\circ$). The axial sites of Mn1 are occupied by a μ -bridging TBC[8] phenolic oxygen atom (O2; $\text{Mn1-O2-Mn2} = 92.3^\circ$) and a coordinated dmf ligand (O10). These atoms define the Jahn-Teller axis which deviates somewhat from linearity ($\text{O2-Mn1-O10} = 165.8^\circ$). The coordination sphere of the octahedral Mn2 is occupied by six oxygen atoms: three TBC[8] phenolic oxygen atoms, O3, O4 and the μ -bridging O2, one coordinated dmf O-atom (O9), a μ -methoxide (O11) and the oximic oxygen atom (O13). The six Mn2-O bond distances lie in the range 1.847 Å - 1.981 Å.

The TBC[8] ligand adopts a conformation that may best be described as a “halfway house” between a double-cone and a pleated-loop, wherein three phenol moieties of the TBC[8] ligand adopt a cone orientation (O1, O7 and O8) whilst the other five resemble a regular pleated loop. The combination of the metal dimer and co-complexed oxime prevents full adoption of either common TBC[8] conformation, which we assume would be sterically disfavoured. Two non-coordinated dmf ligands reside in the resulting partial cavities and various $\text{CH}\cdots\pi$ interactions occur between the dmf ligands and the aromatic systems of the phenol rings of TBC[8]. In the first instance (pleated-loop cavity) the dmf ligand is fully ordered and the interaction between the C36-C41 centroid and H11E is 3.220 Å. The second cavity (partial cone) bound dmf ligand is disordered over two positions and thus the two $\text{CH}\cdots\pi$ interactions are different (2.778 Å and 3.162 Å). The Ph-sao²⁻ ligand orients itself so that the phenyl substituent is arranged nearly coplanar and slightly offset with one of the TBC[8] phenyl components (dihedral angle of 7.67°) indicating a $\pi\cdots\pi$ interaction, albeit the centroid (C15-C20) to centroid (C99-C104) distance is reasonably long (4.125 Å). In addition a $\text{CH}\cdots\pi$ interaction (2.996 Å) exists between an aromatic proton of the oxime phenyl substituent and the centroid of an adjacent TBC[8] phenyl ring. In **1** the TBC[8] ligand is tetra-anionic and four hydrogen bonds exist between the hydroxyl groups of the calixarene lower rim with $\text{OH}\cdots\text{O}$ distances in the range 1.794 Å – 1.922 Å. Analysis of the extended structure of **1** reveals that numerous intermolecular interactions are present. In particular a close contact is observed between the C15 – C20 centroid of one aromatic ring and a methyl group proton (H91A) of a neighbouring molecule ($\text{CH}\cdots\pi$ 2.588 Å). In addition $\text{CH}\cdots\pi$ contacts exist between one of the co-crystallised dmf ligands and an aromatic π system. Once more the dmf is disordered and has been modelled over two positions, each with half occupancy, and relevant contacts of 2.836 Å and 2.977 Å.

A search of the CSD for oxime-bridged transition metal dimers reveals around 200 species, only 5 of which comprise two Mn atoms, with the latter all containing a different oxidation state distribution of manganese ions than in **1**; Mn^{II}_2 ,^{7a} $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}7b}$ and Mn^{III}_2 .^{7c,d,e} Complex **1** is therefore the first reported $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ oxime-bridged dimer.

Solid state dc magnetisation measurements were performed on **1** in the temperature range 290 - 5 K in a field of 0.1 T. The $\chi_{\text{M}}T$ value (Fig. 3A) of $\sim 4.7 \text{ cm}^3 \text{ K mol}^{-1}$ at 290 K is close to the spin-only ($g = 2.00$) value expected for one Mn^{3+} ion and one Mn^{4+} ion of $4.875 \text{ cm}^3 \text{ K mol}^{-1}$. The value increases with decreasing temperature to a maximum value of $7.6 \text{ cm}^3 \text{ K mol}^{-1}$ at 18 K, before dropping to a value of $7.4 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K. This behaviour is indicative of the presence of intramolecular ferromagnetic exchange between the two metal ions, with the low temperature maximum in $\chi_{\text{M}}T$ close to that expected for an isolated $S = 7/2$ ground state ($7.875 \text{ cm}^3 \text{ K mol}^{-1}$). The data can be fitted (solid red line in Fig. 3A) to a simple isotropic Hamiltonian ($H = -2JS_1 \cdot S_2$) to afford $J = +9.81 \text{ cm}^{-1}$ with $g = 1.99$. In addition intermolecular interactions were taken into account in the frame of mean-field

theory, by use of the Curie– Weiss temperature, θ . A Curie-Weiss constant of $\theta = -0.27$ K, was necessary to reproduce the small drop of the $\chi_M T$ product below ~ 18 K. In order to determine the ground state spin, magnetisation data were collected in the ranges 1.8 – 7 K and 1 - 7 T. The data were fitted (solid red lines in Fig. 3B) to a Zeeman plus axial zero-field splitting Hamiltonian (Eqn (1)), assuming only the ground state is populated, affording $S = 7/2$, $g = 1.99$ and $D_{\text{cluster}} = -0.91$ cm $^{-1}$. Ac magnetisation measurements were performed on **1** in the 1.8 – 10 K range in a 3.5 G ac field oscillating at 50 – 1000 Hz. The in-phase (not shown) and out-of-phase (Fig. S1) signals show frequency-dependent behaviour below $T \approx 4$ K indicative of the onset of slow magnetic relaxation, but no peaks. The presence of an out-of-phase signal is diagnostic of single-molecule magnetism (SMM) behaviour and is caused by the inability of **1** to relax quickly enough, at these temperatures, to keep up with the oscillating field.

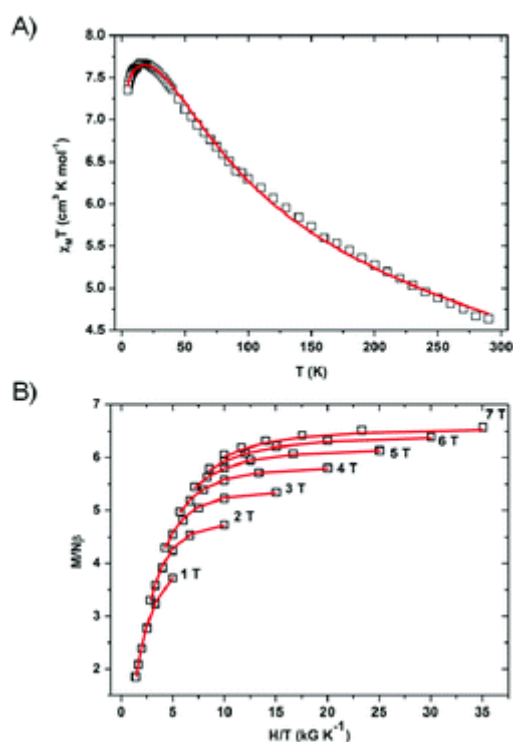


Figure 3. A) Plot of $\chi_M T$ versus T for **1** in 290 - 5 K the temperature range, in an applied field of 0.1 T. B) Reduced magnetisation ($M/N\beta$ versus H/T) data in the 1.8 - 7 K temperature range and 1 - 7 T field range. The solid red lines are the best-fit of the data. See text for details.

$$H = D(\hat{S}_z^2 - S(S+1)/3) + \mu_B g B \hat{S}_z \quad (1)$$

In conclusion we have shown that by using a combination of Ph-saoH $_2$ and TBC[8] the first example of an oxime-bridged Mn $^{\text{III}}$ Mn $^{\text{IV}}$ dimer has been synthesised. Magnetic studies reveal the metal ions to be ferromagnetically coupled and the compound to be a single-molecule magnet.

Notes and references

‡Synthesis of $[M^{III}Mn^{IV}(TBC[8]-4H)(Ph-sao-2H)(\mu_2-OMe)(dmf)_2] \cdot 5dmf$, **1**: TBC[8] (0.1 g, 0.08 mmol), Ph-sao (0.03 g, 0.15 mmol) and $Mn(NO_3)_2 \cdot 4H_2O$ (0.08 g, 0.31 mmol) were dissolved in a mixture of MeOH (6 cm³) and DMF (6 cm³) and stirred for 10 min. Et₃N (0.1 cm³, 0.8 mmol) was added and the reaction stirred for a further hour. Large black crystals suitable for single crystal diffraction studies were obtained in excellent yield (~80%) after slow evaporation of the mother liquor over several days. Elemental analysis calcd (%) for C₁₂₃H₁₆₉N₈O₁₈Mn₂ (2157.54): C 68.47, H 7.90, N 5.19; found: C 68.18, H 7.86, N 5.02. *Crystal data for 1* (CCDC 914769): C₁₂₃H₁₆₉Mn₂N₈O₁₈, $M = 2157.54$, Black Block, $0.40 \times 0.30 \times 0.30$ mm³, triclinic, space group $P-1$ (No. 2), $a = 16.3209(8)$, $b = 19.3140(10)$, $c = 21.1033(10)$ Å, $\alpha = 79.558(2)$, $\beta = 68.960(2)$, $\gamma = 70.483(2)^\circ$, $V = 5837.8(5)$ Å³, $Z = 2$, $D_c = 1.227$ g/cm³, $F_{000} = 2314$, Bruker X8 Apex II CCD Diffractometer, MoK α radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 52.0^\circ$, 85230 reflections collected, 22692 unique ($R_{int} = 0.0443$). Final $GooF = 1.085$, $R_I = 0.0604$, $wR_2 = 0.1630$, R indices based on 16034 reflections with $I > 2\sigma(I)$ (refinement on F^2).

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